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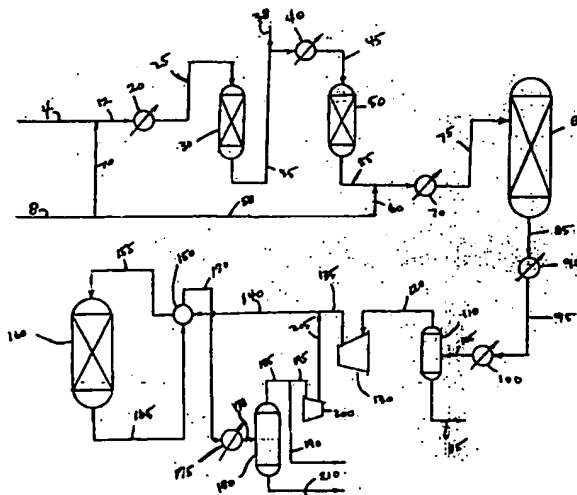
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(54) Title: FUEL COMPOSITIONS COMPRISING NATURAL GAS AND DIMETHYL ETHER AND METHODS FOR PREPARATION OF THE SAME



(57) Abstract: The invention is directed to compositions comprising mixtures of natural gas and dimethyl ether suitable for use as fuel compositions, and particularly to blends of dimethyl ether and a natural gas derived from LNG produced in an LNG process. The dimethyl ether can be added, for example, to a lean natural gas to improve the heat value thereof, and in embodiments, the dimethyl ether is conveniently derived from low value CO₂ contaminants present in a raw natural gas stream used to prepare LNG. Also disclosed are methods to prepare the mixtures.

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FUEL COMPOSITIONS COMPRISING NATURAL GAS AND DIMETHYL ETHER AND METHODS FOR PREPARATION OF THE SAME

Field of the Invention

The present invention relates to fuel compositions derived from natural gas having improved heating values, and in particular to fuel compositions comprising blends of dimethyl ether (DME) and natural gas, including natural gas components derived from liquefied natural gas (LNG), and also to methods for preparation of the fuel blends.

Background of the Invention

Natural gas generally refers to rarefied or gaseous hydrocarbons (comprised of methane and light hydrocarbons such as ethane, propane, butane, and the like) which are found in the earth. Non-combustible gases occurring in the earth, such as carbon dioxide, helium and nitrogen are generally referred to by their proper chemical names. Often, however, non-combustible gases are found in combination with combustible gases and the mixture is referred to generally as "natural gas" without any attempt to distinguish between combustible and non-combustible gases. See Pruitt, "Mineral Terms-Some Problems in Their Use and Definition," Rocky Mt. Min. L. Rev. 1, 16 (1966).

Natural gas is often plentiful in regions where it is uneconomical to develop those reserves due to lack of a local market for the gas or the high cost of processing and transporting the gas to distant markets.

It is common practice to cryogenically liquefy natural gas so as to produce LNG for more convenient storage and transport. A fundamental reason for the liquefaction of natural gas is that liquefaction results in a volume reduction of about 1/600, thereby making it possible to store and transport the liquefied gas in containers at low or even atmospheric pressure. Liquefaction of natural gas is of

even greater importance in enabling the transport of gas from a supply source to market where the source and market are separated by great distances and pipeline transport is not practical or economically feasible.

In order to store and transport natural gas in the liquid state, the natural gas is preferably cooled to -240°F (-151°C) to -260°F (-162°C) where it may exist as a liquid at near atmospheric vapor pressure. Various methods and/or systems exist in the prior art for liquefying natural gas or the like whereby the gas is liquefied by sequentially passing the gas at an elevated pressure through a plurality of cooling stages, and cooling the gas to successively lower temperatures until liquefaction is achieved. Cooling is generally accomplished by heat exchange with one or more refrigerants such as propane, propylene, ethane, ethylene, nitrogen and methane, or mixtures thereof. The refrigerants are commonly arranged in a cascaded manner, in order of diminishing refrigerant boiling point. For example, processes for preparation of LNG generally are disclosed in U.S. Patents 4,445,917; 5,537,827; 6,023,942; 6,041,619; 6,062,041; 6,248,794, and UK Patent Application GB 2,357,140 A. The teachings of these patents are incorporated herein by reference in their entirety. In general, the LNG employed in the practice of the present invention may be prepared according to any of the known LNG processes.

Natural gas produced from some subterranean reservoirs can comprise a very lean gas, i.e., a gas wherein the hydrocarbon content is predominately methane with only relatively minor levels (less than about 3 mol%) of higher hydrocarbons therein such as those boiling greater than methane, typically $\text{C}_2\text{-C}_5$ hydrocarbons. Further, the natural gas industry, including those who produce LNG, typically remove the higher hydrocarbons in the natural gas as produced, and direct them to other uses due to their higher economic value in the marketplace. As a result, when such lean natural gas is used as a feed to produce LNG, the resulting LNG can have an undesirably low heating value,

such as less than 1000 BTU/SCF. Local market demand for LNG typically requires a higher heating value, such as from about 1000 BTU/SCF to about 1200 BTU/SCF and higher.

Historically, to meet the market demand in some markets where increased LNG heating value is desired, the LNG product heating value has been increased by blending it with selected amounts of light hydrocarbons, such as ethane, propane, or butanes, which are most often supplied as a mixture typically referred to as liquefied petroleum gas or "LPG". The amount of LPG blended therein is that sufficient to meet the market specification. This practice may not always be economical for the LNG producer and/or LNG consumer. For example, if the natural gas is very lean or a source of LPG is not readily available at the site where the natural gas is converted to LNG or where the LNG is re-gasified for use by a consumer thereof, then LPG must be shipped to such sites. At present, a significant quantity of LNG is consumed in the Asian Pacific markets and to meet heating value specifications in this market for some LNG products, LPG is shipped long distances for blending with low heat value LNG products. As a result, this practice increases the costs associated with such LNG products.

As can be seen, it would be desirable to develop alternatives so as to improve the heat value of natural gas and in particular, to utilize lean natural gas sources and increase the heat value of LNG produced therefrom without relying on expensive transport of LPG materials. Such alternatives could make such natural gas supplies a more economical and commercially attractive energy resource from the perspective of both LNG producers and consumers.

Summary of the Invention

The foregoing objectives may be attained by the present invention, which in one aspect relates to a composition comprising a blend of natural gas and

dimethyl ether. The composition may comprise a blend of natural gas and dimethyl ether in a liquid form, such as that obtained by condensing both natural gas and dimethyl ether in a LNG process; or in a vapor form, such as that obtained by mixing a regasified LNG product with dimethyl ether in the vapor phase, or by mixing a produced natural gas with dimethyl ether in the vapor phase.

In another aspect, the invention relates to a method for preparing a fuel blend comprising natural gas and dimethyl ether, wherein the method comprises mixing a natural gas component and dimethyl ether.

In embodiments, the method further comprises preparing the natural gas component by the steps of:

pre-treating a natural gas stream comprising acid gases, water and other contaminants therein to remove at least a portion of the contaminants therefrom and provide a natural gas feed;

cooling the natural gas feed in a LNG process to liquefy at least a portion of the natural gas component and thereby produce a LNG product; and

re-gasifying the LNG product to obtain the natural gas component.

In further embodiments of the foregoing, the method also comprises adding the following steps of:

providing dimethyl ether; and

mixing the dimethyl ether with the natural gas component in the vapor phase to obtain the fuel blend.

Where the dimethyl ether and natural gas are mixed in the vapor phase, the dimethyl ether may be added in any amount to achieve a desired higher heating value, provided, however, that the resulting fuel blend will be maintained below the hydrocarbon dew point for the pressure and temperatures at which the fuel blend is to be stored or conveyed, typically those conditions being specified for the pipeline in which the fuel blend is to be conveyed to market or the ultimate user thereof. Typically, the amount of dimethyl ether added will be less than 25 mol% based on the total fuel blend, and beneficially from 10-15 mol% of the total fuel blend.

In the above-described embodiments of the method, it may be convenient to re-gasify the LNG product and mix it with dimethyl ether at a site remote from a location where the natural gas feed originates, and more particularly, at a location near the market for the fuel blend.

In other embodiments where the dimethyl ether is mixed with a natural gas in a LNG process, the method further comprises:

pre-treating a natural gas stream comprising acid gases, water and other contaminants therein to remove at least a portion of the contaminants therefrom and provide a natural gas feed for the LNG process;

mixing the dimethyl ether into the natural gas feed within the LNG process at a temperature above -220°F (-140°C) and in an amount such that the dimethyl ether does not solidify and form a separate solid phase during liquefaction of the natural gas feed in the LNG process;

cooling the resulting natural gas and dimethyl ether mixture within the LNG process to a temperature of from about -240°F (-151°C) to about -260°F (-

162°C) or less so as to liquefy at least a portion of the mixture and thereby produce a blended liquid product at substantially atmospheric pressure; and

re-gasifying the blended liquid product to produce the fuel blend.

Where the dimethyl ether is mixed with the natural gas feed in a LNG process, the mixing may be in the vapor phase, the liquid phase, or both, and the dimethyl ether may be added in an amount to achieve a desired higher heating value when the blended liquid product is regasified, provided, that the amount of dimethyl ether added will not result in solidification of the dimethyl ether in the blended liquid product, typically 5 mol% dimethyl ether or less based on the total blended product.

The blended liquid product according to the foregoing method can be conveniently re-gasified just prior to use to produce the desired fuel blend, and in particular, at a site remote from a location where the natural gas stream originates or the blended liquid product is produced, such as a location near the market for the fuel blend.

In another aspect, the invention is directed to a method for preparing a fuel blend comprising natural gas and dimethyl ether. The method comprises:

pre-treating a natural gas stream comprising acid gases, water and other contaminants therein to remove at least a portion of the contaminants therefrom and provide a natural gas feed;

cooling the natural gas feed in a LNG process to liquefy at least a portion of the natural gas component and thereby produce a LNG product;

providing dimethyl ether;

re-gasifying the LNG product to obtain the natural gas component; and

mixing the dimethyl ether with the natural gas component in the vapor phase to obtain the fuel blend.

In the above-described embodiment, it may be convenient to re-gasify the LNG product and mix it with dimethyl ether at a site remote from a location where the natural gas feed originates or the LNG product is produced, and more particularly, at a location near the market for the fuel blend.

Brief Description of the Drawings

Figure 1 is a schematic process flow sheet illustrating a process for preparing methanol with a feed that includes all or a portion of CO₂ contaminant that may be separated and recovered from a lean natural gas produced from a subterranean reservoir. The methanol may then be reacted to form DME, which in turn can then be mixed with natural gas according to the invention to form a fuel blend composition of higher heat value relative to the lean natural gas.

Figure 2 is a simplified block flow diagram illustrating an embodiment of the present invention, wherein a lean natural gas is blended with DME in the vapor phase and then condensed in a natural gas liquefaction process to produce a blended liquid LNG/DME product. The blended liquid LNG/DME product may then be conveniently transported to a distant market, and later re-gasified at a site remote from the location where the blended liquid product is produced or liquefied to provide a fuel composition with greater heat value relative to the lean natural gas.

Figure 3 is a simplified block flow diagram illustrating another embodiment of the present invention, wherein LNG produced from a lean natural gas and

DME are re-gasified and mixed in the vapor phase to produce a fuel blend according to the invention. The LNG and DME employed may be manufactured at a location where the raw natural gas used to make the LNG is produced from a subterranean reservoir. The LNG and DME can then be conveniently transported to a distant market, and later re-gasified and mixed to provide a fuel blend composition with greater heat value relative to the lean natural gas.

Figure 4 is a table illustrating data in connection with Examples 1-3 and Comparative Examples A-D discussed hereinafter.

Figure 5 is a graph illustrating, on the left-side vertical axis - the higher heating value (HHV) in terms of BTU/scf; and on the right-side vertical axis - hydrocarbon dew point in terms of °F, for various blends of natural gas and DME according to the invention. The line with datapoints illustrated by round dots shows the HHV calculated for various blends. The curve with datapoints shown as squares shows the hydrocarbon dew point at a pressure of 14.7 psia calculated for various blends of natural gas and DME, while the curve with datapoints shown as triangles shows the hydrocarbon dew point calculated at a pressure of 500 psia for the blends.

Detailed Description of the Invention

The natural gas component employed in practicing the present invention may be any light hydrocarbon-containing gas that can be used as a fuel gas, advantageously it is a lean natural gas as previously discussed with a relatively low heating value, such as less than 1000 BTU/scf.

Typically, as mentioned above, there many natural gas reservoirs that contain significant amounts of non-combustible CO₂ gas therein. At present, commercial scale LNG plants use processes which generally require nearly complete removal of acid gases, including CO₂, from the feed gas to the LNG

process. In the past, the CO₂ extracted from the feed gas has been simply vented to the atmosphere. However, current concerns over global warming, internationally driven initiatives to reduce greenhouse emissions, and other environmental factors make venting of such CO₂ undesirable.

In general, where the natural gas component is derived from LNG, the LNG employed in the practice of the present invention may be prepared according to any known LNG process. For example, processes for preparation of LNG generally are disclosed in U.S. Patents 4,445,917; 5,537,827; 6,023,942; 6,041,619; 6,062,041; 6,248,794, and UK Patent Application GB 2,357,140 A, the teachings of which are incorporated herein by reference in their entirety. Another LNG process which is integrated with other processes to produce liquid products from natural gas is also disclosed in co-pending U.S. Patent Application, Serial No. 10/051,425, filed January 18, 2002, wherein flash gas from the LNG process is employed to make other liquid products, such as methanol, dimethyl ether, hydrogen, and Fischer-Tropsch products. The teachings of this application are also incorporated herein by reference in their entirety.

The natural gas feed contemplated herein for use in preparing the LNG in an LNG process generally comprises at least 50 mole percent methane, preferably at least 75 mole percent methane, and more preferably at least 90 mole percent methane. The balance of natural gas as mentioned briefly above generally comprises other combustible hydrocarbons such as, but not limited to, lesser amounts of ethane, propane, butane, pentane, and other higher boiling hydrocarbons, and non-combustible components such as carbon dioxide, hydrogen sulfide, helium and nitrogen.

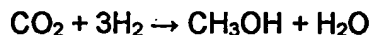
The presence of heavier hydrocarbons such as ethane, propane, butane, pentane, and hydrocarbons boiling at a boiling point above pentane can

optionally be reduced in the natural gas feed to an LNG process through gas-liquid separation steps, in the event such hydrocarbons have greater value for use outside the production of LNG. Hydrocarbon boiling at a temperature above the boiling point of pentane or hexane is generally directed to crude oil. Hydrocarbon boiling substantially at a temperature above the boiling point of ethane and below the boiling point of pentane or hexane is generally removed from the methane feed to the LNG process, and is sometimes considered to be natural gas liquids or "NGLs". These heavier hydrocarbons are also typically removed from natural gas produced from a formation in preparation of a natural gas fuel.

For most markets, it is also desirable to minimize the presence of non-combustibles and contaminants in the LNG or fuel gas, such as carbon dioxide, helium and nitrogen and hydrogen sulfide. Depending on the quality of a given natural gas reservoir (which may contain as much as 50% to 70% carbon dioxide), the natural gas may be pre-processed at a natural gas plant for pre-removal of such of the above components or may be conveyed directly to an LNG plant for pre-processing prior to manufacture of LNG products. Accordingly, the natural gas feed to the LNG process is generally pre-treated, prior to liquefaction in the LNG process, to separate the CO₂ and other acid gases therein. As mentioned below, the CO₂ removed from a natural gas can then be recovered and used to make methanol, and the methanol converted to DME, for use in accordance with the present invention.

Pretreatment generally begins with steps commonly identified and known in connection with conventional LNG production, including, but not limited to, removal of acid gases (such as H₂S and CO₂), mercaptans, mercury and moisture from the natural gas stream, as further discussed herein.

U.S. Provisional Application, Serial No. 60/458,005 filed on March 27, 2003, which is incorporated herein by reference in its entirety, discloses a process for integration of LNG processes with other processes to prepare liquid products from natural gas, such as a methanol production process comprising conversion of the natural gas to synthesis gas (H_2 and CO) and then conversion of the synthesis gas to methanol. In the disclosed process, the non-combustible CO_2 gas separated from the raw natural gas prior to being fed to the LNG process is recovered and subsequently utilized in the production of methanol. The CO_2 can be converted to methanol by any known synthesis method, such as those illustrated for example in Vol. 16, pages 537-556 of the Kirk-Othmer Encyclopedia Of Chemical Technology (4th Ed. - John Wiley & Sons Inc. New York, NY 1995), the teachings of which are incorporated herein by reference. The CO_2 can generally be readily reacted with hydrogen gas using any conventional methanol synthesis catalyst, such as a zinc-chromium oxide catalyst or copper-zinc-alumina catalyst as known in the art, to form methanol according to the following equation:



Hydrogen gas for the conversion may be obtained by taking a portion of the natural gas (either before or after pre-treatment to remove CO_2 and other acid gases, such as H_2S) and reforming it, such as by steam methane reforming, to produce a synthesis gas with a H_2 to carbon oxide ratio favorable for efficient conversion to methanol. Generally, this stoichiometric molar ratio is expressed as follows:

$$S_n = [H_2 - CO_2] / [CO + CO_2]$$

which is generally from 1.5 to 2.5 and more particularly 2.0 to 2.1. As a result, CO_2 which would otherwise have been vented to atmosphere can be

advantageously converted to higher value products, such as methanol and dimethyl ether.

An embodiment of the process disclosed in U.S. Serial No. 60/458,005 is illustrated in Fig. 1. Separation of the CO₂ from the natural gas as produced from a reservoir is not shown on Fig. 1 for convenience, but may be done by any of a number of methods known to the art and is briefly mentioned herein.

Typically, the CO₂ and other acid gases such as H₂S, as well as other contaminants such as mercaptans, mercury and water, are removed in conventional pre-treatment steps. Acid gases and mercaptans are commonly removed via a sorption process employing an aqueous amine-containing solution or other types of known physical or chemical solvents. An inhibited amine solution can be used to selectively remove the CO₂ in the natural gas stream, but not H₂S gas. The H₂S gas can then be removed in a subsequent step. A substantial portion of the water is generally removed as a liquid through two-phase gas-liquid separation prior to or after low level cooling of the natural gas, followed by molecular sieve processing for removal of trace amounts of water. Residual amounts of water and acid gases are most commonly removed through the use of particularly selected sorbent beds such as regenerable molecular sieves. Mercury is removed through use of mercury sorbent beds. The pretreatment of the natural gas generally results in a treated natural gas having a CO₂ content of less than 0.1 mole percent, and more preferably less than 0.01 mole percent, based on the total feed.

As shown in Fig. 1, all or a portion of the CO₂ recovered from such pre-treatment steps may be conveyed by lines 8 and 10 and then combined with a natural gas stream in line 4 to produce a blended feed stream which is conveyed by line 12 to a heater 20. After being heated in heater 20, the blended feed stream is then conveyed by line 25 to a guard bed vessel 30 wherein any

residual amount of sulfur-containing contaminants present in the blended feed stream may be removed by contact with an adsorbent bed, typically of zinc oxide. Alternatively, the CO₂ stream conveyed by lines 8 and 10 and natural gas stream conveyed by line 4 could be treated individually in such guard beds.

After treatment in the guard bed 30, steam is added to the blended feed stream via line 38. The blended feed stream is then conveyed by line 35 to heater 40 wherein the temperature thereof is further adjusted to from 300°C (572°F) to 450°C (842°F) prior to introducing the blended feed stream via line 45 to pre-reformer reactor vessel 50. Pre-reformer reactor vessel 50 typically contains a nickel-based reforming catalyst, but may be any of a number of reforming catalysts as known in the art, and is designed to convert higher hydrocarbons which may be present in the blended feed stream and produce a predominately methane-containing feed stream. Effluent from pre-reformer reactor vessel 50 is conveyed by line 55 to a heater 70 which heats the effluent to a temperature suitable for steam reforming of the methane-containing stream into synthesis gas, typically a temperature of from 400°C (752°F) to 500°C (932°F). In the event that the CO₂ feed in line 8 is substantially free of sulfur-containing compounds, such as less than 1 ppm, it is possible to add CO₂ to the process at the location identified as 60 on Fig. 1, by conveying all or part of the CO₂ to this location via line 58.

After being heated to a temperature suitable for steam reformation, the methane-containing stream is conveyed by line 75 to steam reformer vessel 80. Steam reformer vessel 80 typically contains a nickel-containing steam reforming catalyst, but may be any of those known in the art, which converts the methane-containing stream into one rich in synthesis gas, i.e., hydrogen gas and carbon oxides. The synthesis gas stream exiting steam reformer vessel 80 is conveyed by line 85 to a heat exchanger 90 where excess heat therein is recovered for other uses, such as in heaters 20 and 40. The synthesis gas stream is then

conveyed by line 95 to a cooler 100 wherein the temperature is further reduced. The so-cooled synthesis gas stream is conveyed by line 105 to separator 110 wherein condensed water may be removed from the process by line 115. The synthesis gas stream is thereafter conveyed by line 120 to synthesis gas compressor 130 which compresses the stream to a pressure suitable for methanol production, such as 35 to 150 bar. The compressed synthesis gas stream is then conveyed by lines 135 and 140 to heat exchanger 150 wherein the temperature is adjusted to that suitable for methanol production, such as from 200°C (392°F) to 300°C (572°F).

After adjustment of temperature, the synthesis gas stream is conveyed by line 155 to methanol synthesis reactor 160. Methanol synthesis reactor 160 generally utilizes a catalyst, such as a copper-zinc-alumina catalyst as mentioned above, but may be any of those known in the art. Effluent from the methanol synthesis reactor 160 comprised primarily of methanol, water, and unreacted synthesis gas is conveyed by line 165 to heat exchanger 150 wherein excess heat is recovered therefrom, and thereafter the effluent is conveyed by line 170 to cooler 175. Thereafter, the effluent is conveyed by line 178 to separator 180 wherein a crude methanol product is recovered through line 210 and a gaseous stream exits by line 185. A purge gas stream, which may be used as fuel gas, is taken off via line 190 and the remainder of the gaseous stream comprised of unreacted synthesis gas is directed by line 195 to recycle compressor 200 which recompresses the gaseous stream to that suitable for methanol synthesis as previously described. The compressed gaseous stream is directed by line 205 to line 135 and mixed with fresh synthesis gas.

The resulting methanol product from line 210 can then be purified by methods as known in the art, such as distillation, and then readily converted to DME as summarized on pages 538-539 of the Kirk-Othmer passage previously

incorporated herein. In general, DME is prepared by dehydrating methanol over an acidic catalyst to produce dimethyl ether and water.

While the foregoing process has been described in detail, it should be understood that the DME can be derived from any other source or method known in the art, and that the natural gas component may be derived from LNG or simply comprise natural gas produced from a subterranean reservoir or formation with or without pretreatment to remove contaminants as described herein.

Where the DME is to be incorporated into the feed during the production of LNG products (which may be either in the vapor phase, liquid phase, or both), such that the DME and LNG are condensed in the LNG process to produce a blended liquid product comprised of LNG and DME, as illustrated generally by Fig. 2, the DME employed should be substantially pure DME. By "substantially pure" in this instance, it is meant that there should be less than 0.002 mol% of contaminants therein based on the total DME composition employed for blending, such contaminants typically being water and methanol that are present from the process used to produce the DME and which are typically present in commercial grades of DME. The DME material employed in this embodiment can be distilled until reaching the desired DME purity level. The contaminants generally have a freezing point significantly higher than those of DME and methane, and as such would likely freeze and form an undesirable solid phase in the liquefaction process employed to produce the LNG. Furthermore, while DME has physical properties similar to LPG and might be expected to have a solubility in LNG similar thereto, in practice it has been found that the DME has relatively limited solubility in liquid LNG. Typically, the foregoing method of condensing both DME and LNG by a LNG type process is limited to applications where only a relatively minor change in heat value of the LNG product is desired, such as production of a blended LNG/DME liquid product wherein the amount of DME therein is 5 mol% or less of the total blended product.

In accordance with the foregoing embodiment of the present invention, during production of LNG in a natural gas liquefaction process as previously mentioned, the DME component may be blended into the feed stream to be liquefied in the LNG process at a point after removal of the NGLs, but before the methane gas stream is cooled to about the freezing point of DME, i.e., about -220°F (-140°C). The DME should be blended into the feed stream above a temperature of about -220°F (-140°C) so that a separate, solid phase of DME is not formed in the natural gas feed stream. Also, in this embodiment, it is important to maintain the DME content within feed stream being liquefied below a saturation point so that the DME does not solidify and create a separate solid phase. Generally, this concentration is about 5 mole% based on total amount of blended liquid product.

Fig. 2 illustrates in simple terms the method of blending of DME into natural gas during production of a LNG product in a natural gas liquefaction process according to the embodiment just mentioned.

Mixing of the DME and LNG product in the liquid phase after production of the LNG is not desirable, due to the limited solubility of the DME therein, and also greater tendency of the DME to form an undesirable solid phase.

It is generally more favorable and convenient to mix the DME into a natural gas component in the vapor phase. In this case, the natural gas component may be a natural gas obtained by re-gasification of an LNG product, or it may be a natural gas obtained from another source, such as by production from a subterranean reservoir, with or without the one or more of the pre-treatment steps previously mentioned. If the DME is to be blended with the LNG after re-gasification, then a larger amount of such contaminants can be tolerated so long as the contaminants do not inhibit the intended use of such blend, as in

for example, use as a fuel composition. Also, DME has physical properties similar to LPG, and thus it may be stored as a liquid under pressures similar to those used in connection with storage of LPG. Just prior to use, the DME may be re-gasified, such as by reduction of pressure, and then mixed with the natural gas component. Alternatively, the DME may be directly injected and mixed with the re-gasified LNG.

In accordance with the foregoing embodiment of the invention wherein DME is mixed with a natural gas component in the gas phase, the blending of the DME can be generally accomplished without significant attention to keeping the DME concentration relatively low. Therefore, it is not as important to employ substantially pure DME as previously mentioned herein, and also the concentration of DME blended into the natural gas is not limited to 5 mol%. As such, mixtures having a relatively larger amount of DME mixed with the natural gas component can be prepared by this embodiment. Typically, in commercial practice and as a preferred embodiment of the invention, it would only necessary to blend in enough DME so that the ultimate, blended natural gas product has a higher heating value which meets a consumer's specification, as the DME is a higher value component relative to the natural gas. Typical desired heating values are mentioned herein. More importantly, the upper limit for the amount of DME added will be that which allows the resulting fuel blend to be maintained below the hydrocarbon dew point for the pressure and temperature at which the fuel blend is to be stored or conveyed, typically those conditions being specified for the pipeline in which the fuel blend is to be conveyed to market or the ultimate user thereof. Fig. 5 shows that the hydrocarbon dew point for a selected pipeline pressure varies based on the amount of DME added to the fuel blend. As such, the customer specification can usually be attained by preferably blending in a minor amount of DME, such as less than 25 mol% based on the total fuel composition, generally less than 20 mol%, and beneficially from 15 mol% to 10 mol% due to these considerations. In this embodiment, the DME may be

conveniently added at any temperature up to the applicable dew point of the natural gas component employed so that no liquids condense from the gas phase.

Mixing of the DME and natural gas component in the gas phase according to this embodiment of the invention may be conducted in any process vessel, such as a pipe or tank.

Fig. 3 illustrates in simple terms the blending of DME into a natural gas component derived from LNG in the vapor phase after re-gasification of the LNG at, for example, a re-gasification facility near a market site for such gas product. Re-gasification methods for LNG are generally well-known in the art. Preferably, the DME employed will be stored in a liquid state, which is also more convenient and economical for transport of the DME composition to a market site, and then the DME is re-gasified prior to or during blending with the re-gasified LNG. Re-gasification methods for LNG can also be used to re-gasify the DME. Further, such re-gasification methods can also be used to re-gasify a DME/LNG blend which is in a liquid state according to the aspect of the invention previously mentioned.

A particular blended DME/LNG liquid product, in accordance with the present invention, generally comprises:

- less than 2 mole percent nitrogen and preferably less than 1 mole percent nitrogen;
- less than 1 mole percent and preferably less than 0.5 mole percent helium;
- less than 3 mole percent and preferably less than 1.5 mole percent of the total of nitrogen and helium; and

- less than 5 mole percent and preferably less than 4 mole percent of DME within the blended liquid product.

Where the DME is blended into a regasified LNG product, according to one aspect of the invention, the resulting fuel blend preferably comprises:

- less than 0.3 mole percent nitrogen and preferably less than 0.2 mole percent nitrogen;
- less than 0.2 mole percent and preferably less than 0.1 mole percent helium;
- less than 0.5 mole percent and preferably less than 0.2 mole percent of the total of nitrogen and helium; and
- less than 25 mol% DME, based on the total fuel blend, typically less than 20 mol%, and beneficially from 10 to 15 mol% DME based on the total fuel blend.

A typical gross heating value for the fuel composition produced in accordance with the present invention generally ranges from about 1000 Btu/scf to about 1200 Btu/scf, and more typically from about 1030 Btu/scf to about 1170 Btu/scf, and particularly from about 1050 BTU/scf to about 1150 BTU/scf.

Specific Embodiments of the Invention

The present invention is described in further detail in connection with the following examples, it being understood that the same is for purposes of illustration and not limitation.

Comparative Example A

In Comparative Example A, the heating value of an LNG composition prepared from a lean natural gas composition is determined according to standard measurements and calculations. The LNG is prepared by a cascade-

type LNG process. The composition of the LNG product is shown in the table of Fig. 4, wherein the methane content is shown to be 97.01 mol%, with a small amount of ethane (1.80 mol%) and even smaller amounts of other light hydrocarbons therein. The heating value of the lean natural gas is about 1025 BTU/scf. The column labeled "A" in Fig. 4 contains data associated with Comparative Example A.

Examples 1-2

Examples 1-2 are blends of a substantially pure DME with the LNG product of Comparative Example A, prepared in accordance with the present invention.

For Example 1, the mixing of the DME is conducted by injecting the DME into the LNG process downstream of any heavy hydrocarbon (butane and heavier) removal operation, but upstream of where the LNG temperature is lowered at or below the normal freezing point of pure DME, about -140°C at atmospheric pressure. The LNG and injected DME are mixed well and thereafter cooled to a temperature below -140°C to substantially liquefy the DME and hydrocarbons therein. The amount of DME injected is sufficient to result in a blended liquid product wherein the DME is about 5 mole percent based on the total liquid product. The data for the resulting liquid product is shown on Fig. 4 in the column listed as "Ex. 1". The liquid product is produced at a temperature of about -162°C (-262°F) and substantially atmospheric pressure (14.7 psia).

For Example 2, the DME is blended with re-gasified LNG at a pressure of 500 psia and temperature of about 15°C (60°F). Data for the resulting vapor phase fuel blend is shown in Figure 4 in the column listed as "Ex. 2". Blending at higher temperatures and in the vapor state allows for higher DME blend concentrations without DME solidification as previously described herein.

Comparative Examples B-C

Comparative Examples B-C concern preparation of blends substantially according to the procedures of Examples 1-2, except that propane is blended rather than DME. The columns labeled "B" and "C" in Fig. 4 corresponds to data associated with Comparative Examples B-C.

Example 3

For Example 3, the procedure of Example 2 is substantially repeated, except that the DME is added in an amount sufficient to yield a fuel blend having 10 mol% DME based on the total fuel blend. The data associated with Example 3 is shown in Fig. 4 under the column listed "Ex. 3".

Comparative Example D

For Comparative Example D, the procedure of Comparative Example C is substantially repeated, except that the amount of propane added is an amount sufficient to yield a blend having 10 mol% propane based on the total blend. The data associated with Comparative Example D is shown in Fig. 4 under the column listed as "D".

As can be seen, the present invention relates to alternative products and methods which may be used to provide more economical and convenient fuel compositions having improved heating values.

CLAIMS

1. A composition comprising natural gas and dimethyl ether.
2. The composition of Claim 1 wherein the natural gas is a lean natural gas.
3. The composition of Claim 2 wherein the lean natural gas comprises less than about 3 mol% of C₂ to C₅ hydrocarbons with the balance of the hydrocarbons in the lean natural gas being essentially methane, based on the total composition.
4. The composition of Claim 1 wherein dimethyl ether is present in an amount of less than 25 mol% based on the total composition.
5. The composition of Claim 1 wherein dimethyl ether is present in an amount of less than 20 mol% based on the total composition.
6. The composition of Claim 1 wherein dimethyl ether is present in an amount of from 10 mol% to 15 mol% based on the total composition.
7. The composition of Claim 1 wherein the natural gas is derived from a regasified LNG product produced in an LNG process.
8. The composition of Claim 1 having a heating value of from about 1000 BTU/scf to about 1200 BTU/scf.
9. The composition of Claim 1 having a heating value of from about 1030 BTU/scf to about 1170 BTU/scf.

10. The composition of Claim 1 having a heating value of from about 1050 BTU/scf to about 1150 BTU/scf.

11. A method for preparing a fuel blend comprising natural gas and dimethyl ether, the method comprising mixing a natural gas component and dimethyl ether.

12. The method of Claim 11 wherein the natural gas component is derived from a regasified LNG product prepared in a LNG process.

13. The method of Claim 12 further comprising:

pre-treating a natural gas stream comprising acid gases, water and other contaminants therein to remove at least a portion of the contaminants therefrom and provide a natural gas feed;

cooling the natural gas feed in the LNG process to liquefy at least a portion of the natural gas component and thereby produce a LNG product; and

re-gasifying the LNG product to obtain the natural gas component.

14. The method of Claim 13 further comprising:

providing dimethyl ether; and

mixing the dimethyl ether with the natural gas component to obtain the fuel blend.

15. The method of Claim 14 wherein mixing of the natural gas component and dimethyl ether occurs at a site remote from the location where the natural gas stream originates.

16. The method of Claim 12 wherein the dimethyl ether is blended in an amount such that the concentration of dimethyl ether in the fuel blend is less than 25 mol% based on the total fuel blend.

17. The method of Claim 12 wherein the dimethyl ether is blended in an amount such that the concentration of dimethyl ether in the fuel blend is less than 20 mol% based on the total fuel blend.

18. The method of Claim 12 wherein the dimethyl ether is blended in an amount such that the concentration of dimethyl ether in the fuel blend is from 10 mol% to 15 mol% based on the total fuel blend.

19. The method of Claim 12 wherein the fuel blend has a heating value of from about 1000 BTU/scf to about 1200 BTU/scf.

20. The method of Claim 12 wherein the fuel blend has a heating value of from about 1030 BTU/scf to about 1170 BTU/scf.

21. The method of Claim 12 wherein the fuel blend has a heating value of from about 1050 BTU/scf to about 1150 BTU/scf.

22. The method of Claim 11 further comprising:

pre-treating a natural gas stream comprising acid gases, water and other contaminants therein to remove at least a portion of the contaminants therefrom and provide a natural gas feed for a LNG process;

mixing the dimethyl ether into the natural gas feed within a LNG process at a temperature above -220°F (-140°C) and in an amount such that the dimethyl ether does not solidify and form a separate solid phase during liquefaction of the natural gas feed in the LNG process; and

cooling the resulting natural gas and dimethyl ether mixture within the LNG process to a temperature of from about -240°F (-151°C) to about -260°F (-162°C) or less so as to liquefy at least a portion of the mixture and thereby produce a blended liquid product at substantially atmospheric pressure; and

re-gasifying the blended liquid product to produce the fuel blend.

23. The method of Claim 22 wherein the fuel blend comprises dimethyl ether in an amount of 5 mole % or less based on the total fuel blend.

24. A method for preparing a fuel blend comprising natural gas and dimethyl ether, the method comprising:

pre-treating a natural gas stream comprising acid gases, water and other contaminants therein to remove at least a portion of the contaminants therefrom and provide a natural gas feed;

cooling the natural gas feed in a LNG process to liquefy at least a portion of the natural gas component and thereby produce a LNG product;

providing dimethyl ether;

re-gasifying the LNG product to obtain the natural gas component; and

mixing the dimethyl ether with the natural gas component to obtain the fuel blend.

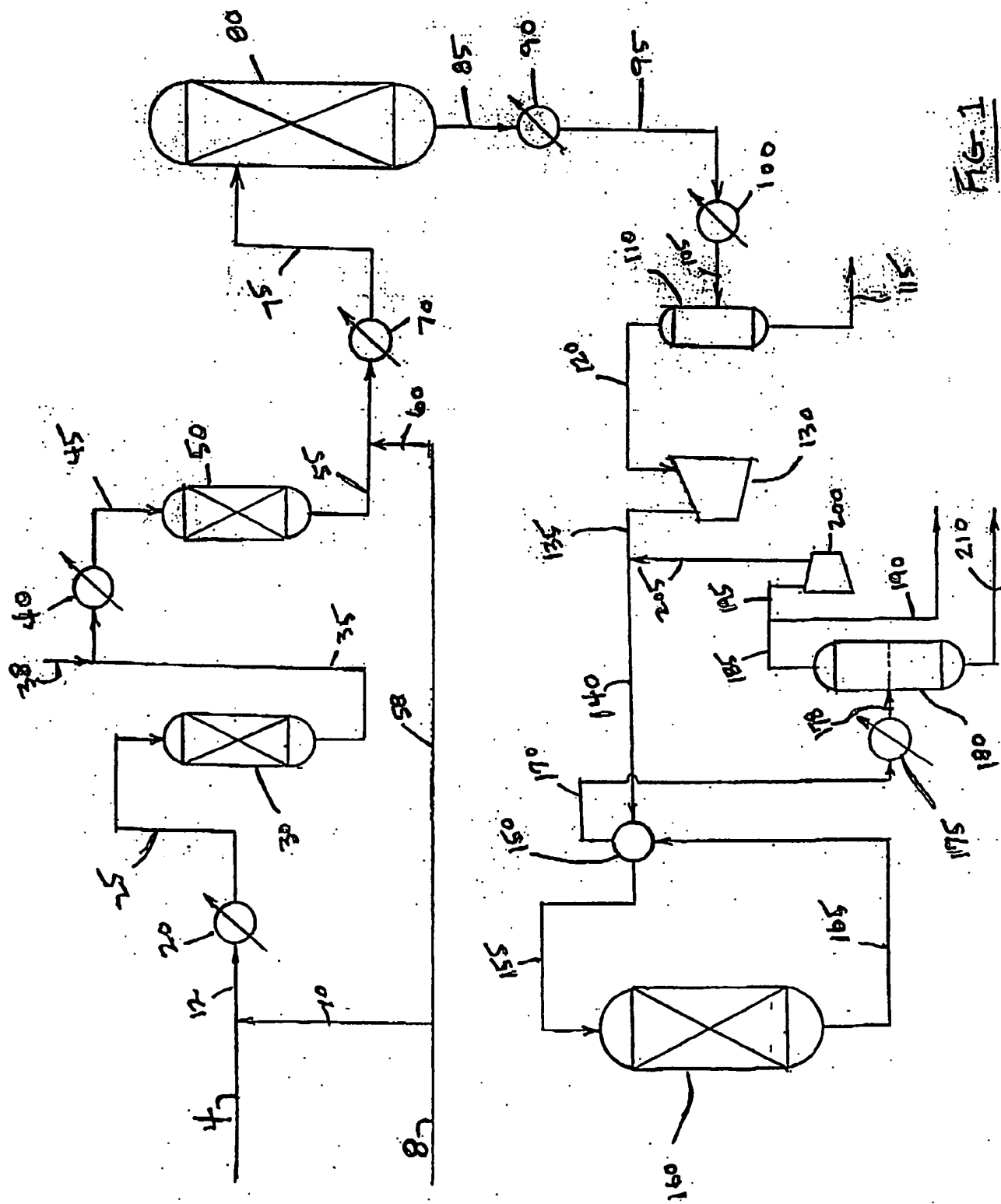


FIG. 1

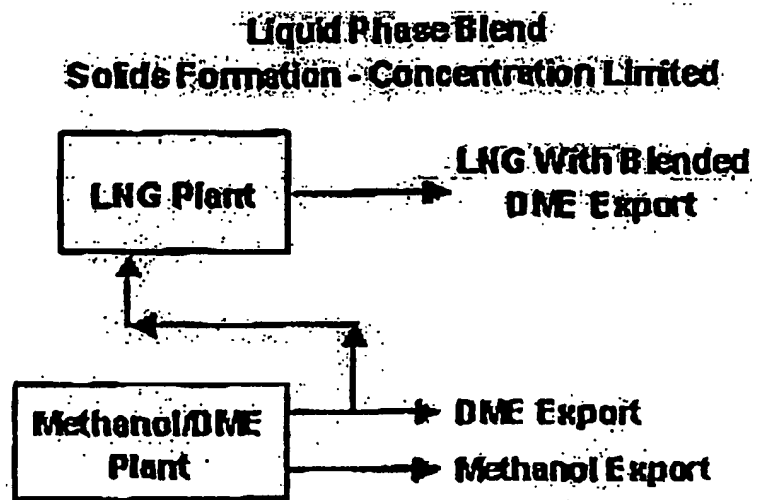


Fig. 2

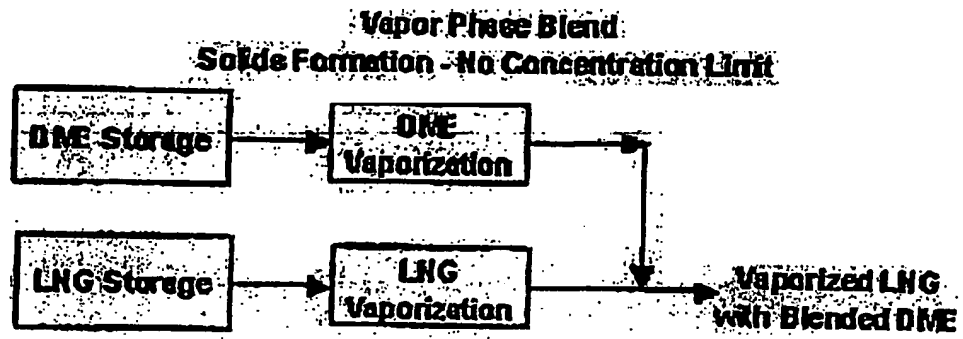
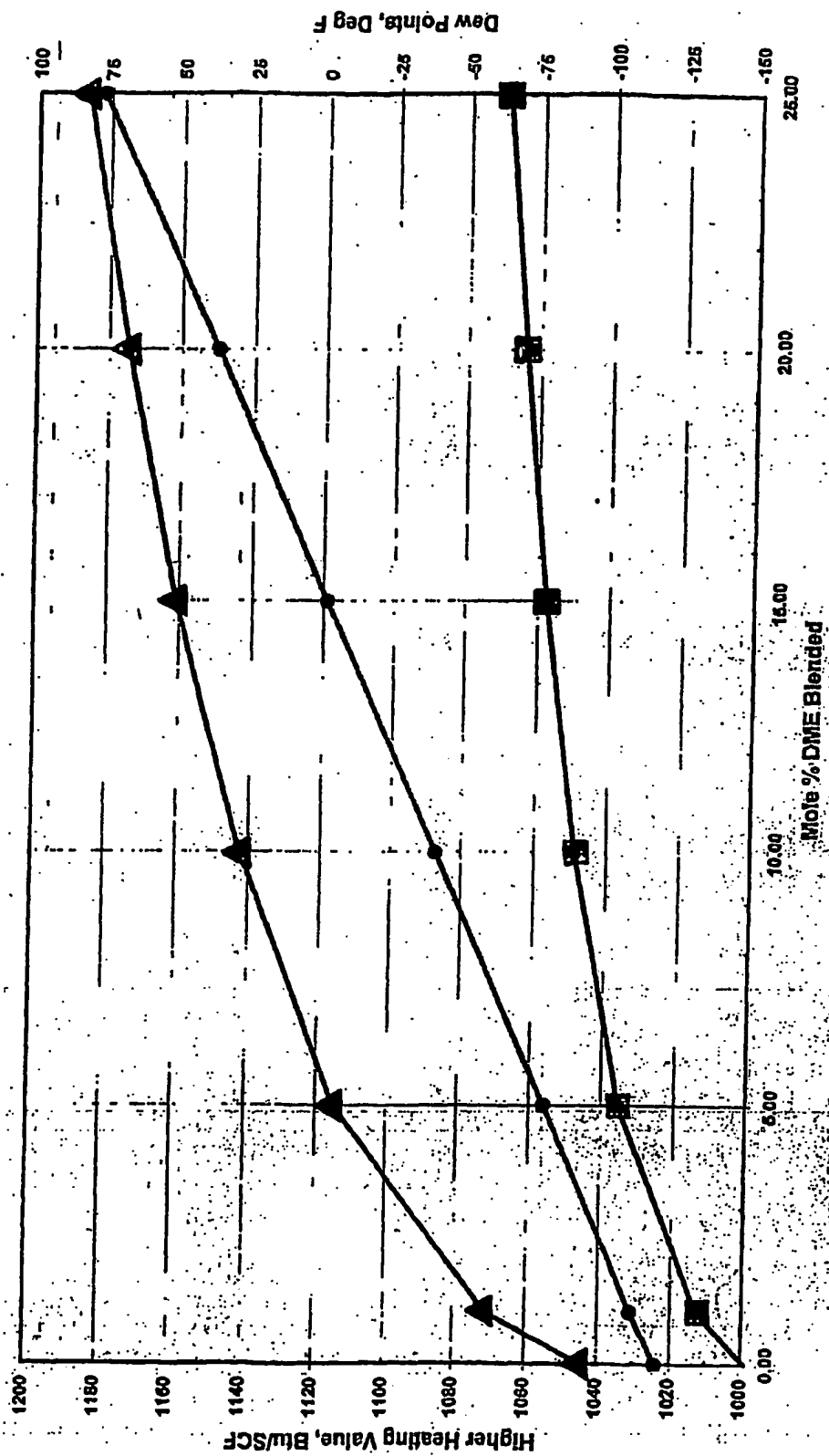


Fig. 3

	Blending Cases						
	A	Ex. 1	Ex. 2	B	C	Ex. 3	D
Criteria	LNG	LNG+5% DME	LNG+5% DME	LNG+5% Propane	LNG+10% DME	LNG+10% DME	LNG+10% Propane
Higher Heating Value, Btu/SCF	1025	1058	1058	1100	1100	1088	1174
Pressure [psia]	14.686	14.686	600	14.686	600	500	500
Temperature [F]	-262	-262	60	-262	60	60	60
Mixture Phase	Liquid	Liquid	Vapor	Liquid	Vapor	Vapor	Vapor
Bubble Point Temperature [F]	-262	-262	-130	-262	-128	-127	-125
Dew Point Temperature [F]	-151	-108	-7	-129	-33	27	-3
Compositions							
Component	Mole Percent	Mole Percent	Mole Percent	Mole Percent	Mole Percent	Mole Percent	Mole Percent
Nitrogen	0.70%	0.67%	0.67%	0.67%	0.63%	0.63%	0.63%
Methane	97.01%	92.16%	92.16%	92.16%	87.30%	87.30%	87.30%
Ethane	1.80%	1.71%	1.71%	1.71%	1.62%	1.62%	1.62%
Propane	0.34%	0.32%	0.32%	5.32%	0.31%	0.31%	10.31%
i-Butane	0.07%	0.06%	0.06%	0.08%	0.06%	0.06%	0.08%
n-Butane	0.08%	0.07%	0.07%	0.07%	0.07%	0.07%	0.07%
i-Pentane	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
n-Pentane	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
n-Hexana Plus	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
Dimethyl ether (DME)	0.00%	5.00%	5.00%	0.00%	0.00%	10.00%	0.00%
Molecular Weight	18.54	18.01	18.01	17.92	18.48	18.48	19.29

Fig. 4

LNG-DME Blending HHV & HC Dew Points



● HHV, Btu/SCF ■ HCDP @ 14.7 psia ▲ HCDP @ 500 psia

Fig 5

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2004/008780

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C10L3/00 C10L3/10		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C10L		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, PAJ, COMPENDEX		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 2 765 238 A (RENAULT) 31 December 1998 (1998-12-31) page 5, line 1 - line 4; claim 5	1-24
A	US 6 023 942 A (COLE ERIC T ET AL) 15 February 2000 (2000-02-15) cited in the application column 4, line 33 - line 60; claim 1	11-24
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<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search <div style="text-align: center; font-weight: bold;">27 July 2004</div>		Date of mailing of the international search report <div style="text-align: center; font-weight: bold;">06/08/2004</div>
Name and mailing address of the ISA European Patent Office, P.B. 6818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016		Authorized officer <div style="text-align: center; font-weight: bold;">Bertrand, S</div>

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2004/008780

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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JP 11293263	A	26-10-1999	NONE	

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